Feasibility of Heterogeneous Batch Distillation Processes

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Synthesis of heterogeneous batch distillation is discussed, which aims at splitting azeotropic mixtures by adding an entrainer partially miscible with one of the initial binary mixture components. Key operational parameters are identified such as the amount of entrainer added in the ternary feed, the reflux policy, and the vapor line position by examples. Synthesis and operation are less straightforward for heterogeneous batch distillation than those for the homogeneous case, but offer many advantages: more design alternatives, simplified distillation sequences, a lower consumption of entrainer, and a crossing of distillation boundaries by the still path. Feasibility is assessed using simplified modeling and confirmed using a commercial batch process simulator package. Synthesis expectations and simulated results are verified throughout bench-plant experiments for the separation of the acetonitrile—water mixture using acrylonitrile as a light heterogeneous entrainer.

Introduction

Batch distillation is a significant process because of the operational flexibility that it offers. It is particularly suitable for the pharmaceutical and specialty chemical industries where products have a high added value and are usually quite diverse and in small quantities. Batch distillation is also used for solvent recovery and through this application assists in dealing with increasing economic incentives and environmental regulations. Azeotropes in multicomponent equilibrium diagrams associated to waste-solvent streams complicate both synthesis and design steps of batch distillation processes. Indeed, an azeotropic ternary diagram may display distillation boundaries that outline distillation regions. Hence, batch distillation product sequence depends on the initial feed location in the equilibrium diagram. Therefore, the separation of a binary mixture into its pure components may require several batch distillation tasks or even be unfeasible. One way to circumvent an azeotrope is to add an entrainer that interacts preferentially with one of the binary components.

The choice of a suitable entrainer is an essential step, because it significantly affects the process duration and its economic performance. In particular, it defines the sequence of batch distillation tasks that enable the separation of the original components with the desired purity. This issue was first tackled by Bernot et al. (1991) and Düssel and Stichlmair (1995) for homogeneous batch azeotropic distillation. Those authors devised several entrainer selection rules that are correct, but remain incomplete. In contrast, no specific, no specific entrainer selection rules had been reported for heterogeneous batch distillation. Heterogeneous batch distillation consists in adding a component which causes a liquid-liquid phase split over an extensive range of composition. In two recent articles, we have established a complete set of rules for the selection of both homogeneous and heterogeneous entrainers for the separation of minimum or maximum temperature azeotropic binary mixtures or low relative volatility components from the analysis of ternary residue curve diagrams under assumptions of high number of trays and total reflux/reboil ratio (Rodriguez-Donis et al., 2001a,b). Rules concern the entrainer and the original binary mixture components. They are made of a combination of four general conditions related to their ability to form together binary and/or ternary azeotropes (homogeneous or heterogeneous) and of

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information about their boiling points order. The stability of all fixed points of the system is also required for the determination of the ternary diagram from which the synthesis of the process will be performed. In the heterogeneous case, a feasible entrainer leads to a ternary diagram where the two original components are, or are not, in the same batch distillation region and either the heterogeneous azeotrope or one of the original components is a node. When the heterogeneous azeotrope is an unstable node, a batch rectifier as the first batch task is the preferred choice as it leads to the lowest number of batch tasks needed to obtain a sequence of high purity products. Conversely, a stripper or a rectifier batch process can be used when the original component is an unstable node or a stable node, respectively.

Design and synthesis tools for homogeneous or heterogeneous batch distillation involves the analysis of residue curve maps. The product sequence depends on the initial feedstream location in the ternary diagram. By definition of a batch distillation region, any initial composition inside a given region will lead to the same sequence of products. For homogeneous systems, several algorithms have been established to find batch distillation regions, as well as the still and product paths associated with, considering batch rectifying and stripping columns (Bernot et al., 1990, 1991; Safrit and Westerberg, 1997a,b; Ahmad and Barton, 1996; Ahmad et al., 1998). At first, synthesis tools for homogeneous batch distillation seems to be useful for heterogeneous systems. The heterogeneous region is introduced on the residue curve map through the liquid-liquid boiling envelope determined from liquid-liquid-vapor equilibrium data (Pham and Doherty, 1990a) and the still path and the product sequence is obtained according to the homogeneous scheme.

The only works on heterogeneous batch distillation are from Stichlmair and coworkers (Düssel and Stichlmair, 1995; Stichlmair and Fair, 1998; Warter et al., 1999) and Köhler et al. (1995). The first authors attempted to use homogeneous batch distillation synthesis methods for a heterogeneous system but, as we shall see, this leads to an ambiguous operation of the column. Köhler et al. (1995) presented experimental results of heterogeneous batch distillation, without citing their products. They showed that the still path did not behave at all like in the homogeneous case, but that the process was able to recover in a single rectification step the original azeotropic mixture components that were in two different batch distillation regions.

The objective of this article is to study the performance of heterogeneous batch distillation (HBD) for the separation of minimum azeotropic mixtures, based on a feasibility analysis. As we have shown in previous articles, the feasibility method can also be applied for the separation of maximum boiling azeotropes and close boiling components (Rodriguez-Donis et al., 2001b,c). The influence of the most important operational parameters such as the amount of entrainer added in the ternary feed, the reflux policy through the ratio of the decanted phases in the column reflux, and the position of the vapor line are analyzed and illustrated by several examples.

Feasibility of Homogeneous Batch Distillation Process

Homogeneous batch distillation generally proceeds as follows. An initial mixture is fed to the column and heated to its boiling point. Then, the column is operated at total reflux for some time before distillate is drawn off. Notice that during the total reflux operation, composition changes in the column can be quite large depending on the liquid holdup retained in the trays. For homogeneous batch distillation synthesis, Van Dongen and Doherty (1985) extended the innovative work of Doherty and Perkins (1979) on the structure of residue curve maps for the synthesis of batch distillation processes. Based on the concept of batch distillation region, they defined a general methodology for finding the still path and the product sequence under conditions of total reflux and high number of trays. Bernot et al. (1990, 1991) applied this theory for the synthesis of ternary and quaternary mixtures considering a batch rectifying (stripping) column. For straight distillation boundaries, the unstable (stable) node is the first distillate (bottom) cut and the following cuts can be defined by saddle points and the stable (unstable) node. Then, the still path can be predicted under the limiting operating conditions: the still composition moves along a straight line until it hits a stable (unstable) separatrix. The tangent to the line joining the initial ternary point and the unstable node in the relevant batch region then defines the still path direction. As it reaches a stable (unstable) separatrix, it readily turns and follows this distillation boundary toward the highest (lowest) boiling point vertex of the relevant batch distillation region. The column liquid profile can be approximated as a residue curve that links each punctual still (reflux drum) composition value with the corresponding distillate (bottom) composition. At any time, the product cut composition is collinear to the still path tangent. Boundary curvature may lead to a different product sequence (Bernot et al., 1991). Ahmad and Barton (1996) further extended the use of residue curve maps for the analysis of multicomponent homogeneous batch distillation process.

Safrit et al. (1995) extended the method of Wahnschafft et al. (1992), and Wahnschafft and Westerberg (1993) to deal with the feasibility of continuous distillation (conventional and extractive) to devise feasible product and possible column profile regions. Key differences exist between continuous and batch distillation. In batch distillation the still and products compositions change vs. time; therefore, any feasibility analysis is only valid for a given time. Besides, the still composition is a tray composition and must lie on the column liquid profile just like any other tray composition. Safrit and coworkers showed that the instantaneous region of all feasible liquid profiles at various combinations of reflux and number of trays for a specified still composition is bounded by the total reflux curve and by the tangent to the residue curve through the still composition. The total reflux curve is close to the residue curve linking the product composition x_D to the instantaneous still composition x_S whatever the numbers of trays. The tangent to the residue curve defines the distillate compositions whose product pinch point curve passes through the still composition for an infinite number of trays and a minimum reflux ratio. Safrit et al. (1995) also addressed the same issue for extractive batch distillation, that is, a batch distillation with a continuous feeding of entrainer. Taking into account the mass balance for the extractive section, a Δ point is calculated where all operating lines intersect. The tangent lines to the residue curves drawn from the point Δ determine the pinch point curve Δ. Then, the points Δ, $\boldsymbol{x}_N$, $\boldsymbol{y}_N$ and $\boldsymbol{y}_{N+1}$ are inevitably located on the same operating line, which gives the possible pinch points. Hence, they showed that the unfeasible region is bounded by the pinch point curves and the edges of the ternary diagram. However, Lelkes et al. (1998a) showed that most of the pinch points found by Safrit et al. (1995) were not necessarily pinch points because the equality of equilibrium and arriving vapor compositions that defines a pinch was not always achieved. The feasibility of extractive batch distillation process in a batch rectifier was presented by Lelkes et al. (1998a,b) and Lang et al. (1999, 2000a,b). The feasibility of the process is based on the analysis of the still path on the map of residue curves and the liquid profile in each section of the column. The method involves simplifying assumptions of quasi-steady state in the column and constant molar overflow. Feasibility means that starting from the initial charge under some operating conditions, there is during the whole process at least one extractive column profile connecting the still path with the rectifying column profile that ends at the specified distillate composition. The extractive profile map then enables to draw the real infeasible regions, quite different from the pseudo infeasible regions devised by Safrit et al. (1995). The results obtained from this simplified analysis were corroborated by rigorous simulation and both were in correspondence with experimental results.

Feasibility of Heterogeneous Batch Distillation Process

The feasibility study in batch distillation is based on the analysis of the still path on the residue curve map and of the column liquid profile inside the column. This is usually performed by solving a mathematical model of the process with several assumptions: constant molar overflow and quasi-steady state in the column due to negligible liquid and vapor holdup on the trays. This simplified model allows the determination of the basic pattern of the still, trays, and distillate compositions for preliminary design and synthesis and has been quite successful. Since our purpose is to provide a qualitative understanding of HBD, we keep those same hypotheses to develop our model.

Still path

Heterogeneous batch distillation is shown in Figure 1. A decanter is connected to a regular batch distillation column able to handle liquid-liquid phase split on its trays. We consider the separation of a minimum boiling temperature homoazeotrope using a heterogeneous entrainer which is added initially to the binary azeotropic mixture and forms with one of the components to separate a binary hetroazeotrope which is the only unstable node in the system. The initial ternary mixture is charged into the still and a first operation step is performed at total reflux until the column reaches steady state. Provided that the column has a high enough number of trays, the overhead vapor (V, y_2) boils overhead and is completely condensed in an overall liquid phase L^o whose composition x^o is equal to the unstable heteroazeotropic point composition. A liquid-liquid phase split occurs in the decanter at a specified temperature giving two liquid phases in equilibrium: an entrainer-rich phase L_R with a composition x_R and an entrainer-weak phase L_W with a composition x_W. We consider below that the light and heavy L_L and L_H correspond, respectively, to L_R and L_W. In our analysis we define the molar splitting ratio ω of the light phase to the overall liquid phase L^o equal to V.

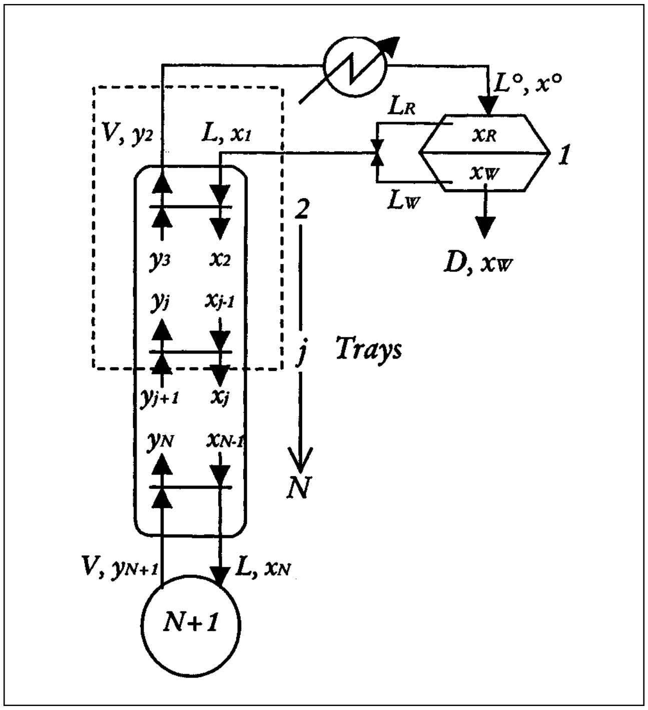

Figure 1. Heterogeneous batch distillation column.

$$L_L = \omega V \text{ and } L_H = (1 - \omega)V \tag{1}$$

The splitting ratio ω in the decanter is defined by the position of the binary heteroazeotrope composition on the conodale.

When the distillation step starts, a distillate is withdrawn with the same composition than phase L_W. A distinct feature of heterogeneous distillation is that the liquid reflux (L) to the column can be a combination of both phases L_R and L_W. Such a flexible reflux policy affects the still path and the liquid profile established in the column at total reflux. The influence of the reflux policy on the performance of HBD is analyzed below.

HBD feasibility means that during the whole process, there exists at least one liquid profile connecting each punctual composition x_S on the still path with the liquid composition leaving the first tray x_1. Also, the vapor composition y_2 in equilibrium with x_1 must lie in the immiscibility gap at the decanter temperature. At first, during the total reflux operation, a column liquid profile will connect the initial still composition to the overhead vapor composition, which is likely close to the heteroazeotrope if the initial composition is located in the same basic distillation region than the unstable binary heteroazeotrope. When the distillation step begins, the feasibility condition has to be achieved through the liquid reflux policy at the top of the column.

Several reflux policies can be thought of classified in two categories:

1. The entrainer-rich phase only is refluxed. The distillate flow rate D equals the entrainer-weak phase flow rate contained in the condensed vapor $D=(1-\omega)\cdot V$. The reflux flow rate can be:

1.1. Equal to the entrainer-rich phase flow rate contained in the condensed vapor L^o. In this case, the entrainer-rich phase volume in the decanter stays at its level at the end of the total reflux operation. $L=\omega\cdot V$.

1.2. A fraction θ of the entrainer-rich phase flow rate contained in the condensed vapor L^o. In this case, the entrainer-rich phase volume in the decanter increases above its level at the end of the total reflux operation. $L=\theta\cdot\omega\cdot V$ and $0<\theta<1$.

1.3. A fraction θ greater than the entrainer-rich phase flow rate contained in the condensed vapor L^o. In this case, the entrainer-rich phase volume in the decanter decreases below its level at the end of the total reflux operation. $L=\theta\cdot\omega\cdot V$ but $\theta>1$.

2. A combination of an entrainer-rich phase and an entrainer-weak phase is refluxed. The entrainer-weak phase flow rate is a fraction φ of the entrainer-weak phase contained in the condensed vapor flowrate L^o; the remaining is removed as distillate D. $0<\varphi<1$ and $D=(1-\varphi)\cdot(1-\omega)\cdot V$. The refluxed entrainer-rich phase flow rate L can be:

2.1. Equal to the entrainer-rich phase flow rate contained in the condensed vapor L^o. In this case, the entrainer-rich phase volume in the decanter stays at its level at the end of the total reflux operation. $L=\omega\cdot V+\varphi\cdot(1-\omega)\cdot V$.

2.2. A fraction θ of the entrainer-rich phase flow rate contained in the condensed vapor L^o. In this case, the entrainer-rich phase volume in the decanter increases above its level at the end of the total reflux operation. $L=\theta\cdot\omega\cdot V+\varphi\cdot(1-\omega)\cdot V$ and $0<\theta<1$ and $0<\varphi<1$.

2.3. A fraction θ greater than the entrainer-rich phase flow rate contained in the condensed vapor L^o. In this case, the entrainer-rich phase volume in the decanter decreases below its level at the end of the total reflux operation. $L=\theta\cdot\omega\cdot V+\varphi\cdot(1-\omega)\cdot V$ but $\theta>1$ and $0<\varphi<1$.

In the most general case, with parameters θ and φ, the variation of the still composition vs. time can be calculated from the material balances

$$\begin{aligned}\frac{dH_s}{dt}&=L-V\\&=\theta\cdot\omega\cdot V+\varphi\cdot(1-\omega)\cdot V-\left[\omega\cdot V+(1-\omega)\cdot V\right]\\&=(\theta-1)\cdot\omega\cdot V-(1-\varphi)\cdot(1-\omega)\cdot V\\&=(\theta-1)\cdot\omega\cdot V-D\end{aligned}\tag{2}$$

$$\begin{aligned}\frac{d(H_s\cdot x_s)}{dt}&=L\cdot x_1-V\cdot y_2\\&=\theta\cdot\omega\cdot V\cdot x_R+\varphi\cdot(1-\omega)\cdot V\cdot x_W\\&\quad-\left[\omega\cdot V\cdot x_R+(1-\omega)\cdot V\cdot x_W\right]\\&=(\theta-1)\cdot\omega\cdot V\cdot x_R-(1-\varphi)\cdot(1-\omega)\cdot V\cdot x_W\\&=(\theta-1)\cdot\omega\cdot V\cdot x_R-D\cdot x_W\end{aligned}\tag{3}$$

with $\theta>0$ and $0<\varphi<1$ and $D=(1-\varphi)\cdot(1-\omega)\cdot V$

Expanding Eq. 3 while substituting Eq. 2 leads to the still path equation

$$\frac{dx_s}{dt}=\frac{(1-\theta)\cdot\omega\cdot V}{H_s}(x_s-x_R)+\frac{D}{H_s}(x_s-x_W)\tag{4}$$

Equation 2 states that the still composition is only influenced by the vapor overflow leaving the column V and by the liquid reflux L going into the column. Through L, the still path depends on the reflux policy established for the distillation step.

Figure 2 illustrates this concept for cases 1.1., 1.2., and 1.3. where the reflux is an entrainer-rich phase only ($\varphi=0$ and $D=(1-\omega)\cdot V$). We discuss the separation of a minimum boiling azeotrope A-B with a low boiling entrainer E. The heteroazeotrope A-E is the unstable node of the system and boils overhead before splitting in the decanter in two liquid phases, each one with a high concentration of E (x_R) or A (x_W).

For case 1.1. ($\theta=1$), Eq. 4 shows that the still composition moves away from the point x_W. Therefore, the still path follows a straight line determined by the charge initial composition and the composition of the original component-rich phase x_W until it reaches an edge or a vertex of the triangle.

For case 1.2. ($0<\theta<1$), Eq. 4 shows that the still path is restricted by a vector cone swept out by two vectors: (x_s-x_W) (which points in the direction away from the entrainer-weak phase) and (x_s-x_R) (which points in the direction away from entrainer-rich phase). The actual direction is given by the relative weights on these vectors. This concept is illustrated in Figure 2b.

For case 1.3. ($\theta>1$), Eq. 4 shows that as in the previous case, a vector cone bounds the region of possible still pot composition movement. However, in this case, the vector (x_R-x_s) points in the direction toward the entrainer-rich phase. And the overall still path direction is different from case 1.2.

For cases 2.1, 2.2, and 2.3, a fraction φ of the entrainer-weak phase is refluxed in addition to the entrainer-rich phase. The behavior of the still path is identical to cases 1.1, 1.2, and 1.3, but the still composition changes more slowly because the distillate flow rate is now reduced by a fraction φ and $D=(1-\varphi)\cdot(1-\omega)\cdot V$.

Overall, the reflux policy of HBD allows us to steer the still pot composition like in extractive distillation or in a middle vessel column by varying the relative weight of both vectors that restrict the still path. A 180° vector cone can be examined theoretically. This can allow in particular to recover B, the component miscible with the entrainer in the still at the process end.

Column profile

Finding an instantaneous feasible profile of the batch column linking the distillate composition to the still composition is not enough. Rather, this necessary and sufficient condition must be achieved for the whole process. Once the still path is established, all feasible column profile must be determined for the given product purity and specified operational parameters. This calculation has to be made for both operational steps of the HBD process: total reflux operation and distillation using a finite reflux ratio. A material balance is estab-

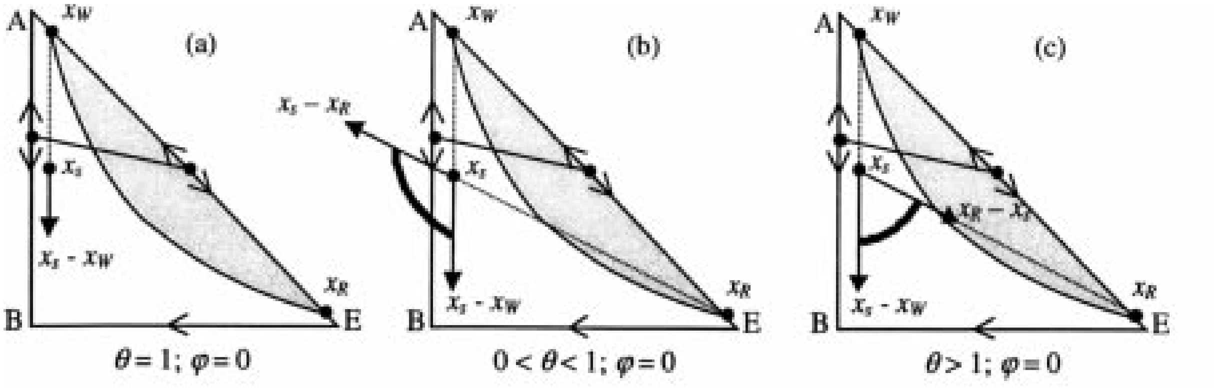

Figure 2. Possible still composition movement at a given point in time.

Only entrainer-rich phase is refluxed.

lished with the same assumptions than above between an arbitrary plate j in the rectifying section and the column top (Figure 1). The component material balance is written using an approximated differential model (Van Dongen and Doherty, 1985) considering a first-order Taylor formula. Such a mathematical model reduces the problem complexity and enables a direct comparison with the simple distillation residue curves

$$\frac{dx_{i,j}}{dh} = x_{i,j} - x_1 + \frac{V}{L} \cdot (y_2 - y_{i,j}) \tag{5}$$

Equation 5 can be applied for both total reflux and distillate removal operation.

Column profile at total reflux operation. In the total reflux case for the rectifying column $V/L = 1$ and, as all condensed vapor is recycled at the top of the column, then $y_2 = x_1$. We consider that the column has a high enough number of trays for the heteroazeotrope to boil overhead ($y_2 = y_{azeo}$). Therefore, the liquid column profile is defined as

$$\frac{dx_{i,j}}{dh} = x_{i,j} - y_{i,j} \tag{6}$$

Equation 6 is equivalent to the simple distillation residue curve equation (Doherty and Perkins, 1979). Indeed, for preliminary design and synthesis of homogeneous batch distillation, the column profile at total reflux can be approximated by a simple distillation residue curve. This approach remains valid for HBD for the portion of the column profile located in the homogeneous region. However, when the liquid composition gets into the heterogeneous region, the column profile at total reflux deviates from the residue curve that would exist if the system were homogeneous for several reasons.

First, inside the heterogeneous region, any liquid composition on a tie line is in equilibrium with a vapor composition that is restricted to lie on a single vapor line. This vapor line terminates at the vapor composition in equilibrium with the liquid-liquid-vapor boiling envelope critical point (Pham and Doherty, 1990b). Heterogeneous residue curves are defined by an equation similar to Eq. 6, but with $x_{i,j}$ being now the overall liquid composition. Besides, as pointed out by Pham and Doherty (1990b), both the heterogeneous residue curve and the vapor boil-off curve must pass through any heterogeneous azeotrope and are tangent to each other at such a fixed point. Consequences are that knowing the separatrix direction near the hetroazeotrope hints at the direction of the vapor line. In all cases, the vapor line lies on the convex side of the distillation boundary because of the tangency condition. Finally, both curves coincide exactly only when the distillation boundary is linear.

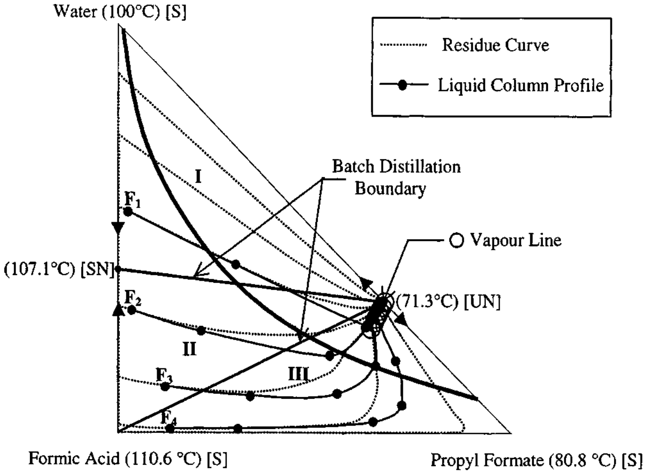

Figure 3. Separation of water–formic acid by heterogeneous batch distillation with propyl formate.

Heterogeneous binary azeotrope case showing the influence of vapor line on the column liquid profile at total reflux.

Second, at total reflux, the liquid stream composition $x_{i,j}$ leaving tray j and the vapor composition $y_{i,j+1}$ of the stream arriving to this same tray are equals. This implies that in the heterogeneous region, the overall liquid leaving tray j lies on the vapor line. These properties show that the liquid profile must approach the heteroazeotrope along the vapor line. As a consequence, the column profile may cross a batch distillation boundary in a way that is not possible in homogeneous batch distillation. Notice that, at finite reflux, the distance between both column vapor and liquid profile will depend on the reflux ratio used during the operation.

Figure 3 displays four column liquid profiles obtained at total reflux for the ternary mixture propyl formate-water-formic acid. The hetroazeotrope propyl formate-water is the only unstable node and will always be obtained as the first distillate cut if a relevant finite reflux ratio and a sufficient number of trays are assessed. Four initial still composition points F_1, F_2, F_3, and F_4 located in three different batch distillation regions (I, II, and III) are chosen. It can be seen that the location of the vapor line in the ternary diagram constrains the liquid profile at total reflux, which must connect the still composition with the equilibrium liquid composition corresponding to the heterogeneous azeotrope. Unlike homogeneous system, the liquid profile diverges from the residue curve. The deviation is more pronounced for the compositions closest to the heterogeneous region, and it also depends on the curvature of the homogeneous residue curve. Indeed, once the liquid profile lies in the heterogeneous envelope, the liquid compositions coincide with the vapor line until they arrive at the heteroazeotrope. In the cases of feed F_1, F_2, and F_3 situated in batch regions I and II, the liquid profile crosses a homogeneous batch distillation boundary and continues in batch region III because the vapor line lies in this region.

When the distillation step begins, one of the decanter liquid phases is taken off as distillate while the other phase or a combination of both liquid phases is refluxed to the column head. Whatever the reflux policy, the liquid reflux composition is different from the condensed vapor composition that made the reflux composition during the total reflux operation. This will affect the liquid profiles shapes besides the fact that the still composition now evolves because of a distillate. Equation 4 can be used to determine the column profile considering any reflux policy established above.

Column profile at defined reflux policy. We have hinted that the reflux policy is more versatile for HBD than for homogeneous batch distillation. Indeed, the liquid reflux composition will be different from the condensed vapor composition when a distillate is removed because any combination of both decanted phases can be used for the reflux. Notice that such a flexibility will likely pose some control problems, one of them being the possible drying of one of the phases into the decanter. Such an operating flexibility demonstrates an advantage of batch vs. continuous distillation.

In heterogeneous continuous distillation, there is a more restricted reflux policy to be used because the top and bottom products composition and the feed tray have to lie on a material balance line (Pham and Doherty, 1990a). Pham and Doherty (1990c) suggested that the liquid reflux overall composition is located on the tie line between the condensed vapor x^o and an entrainer-rich phase composition x_R. Consequently, the liquid composition that leaves from the top tray of the column is placed in the same basic distillation region than the bottom product. If this is not the case, the rectification and stripping profiles do not intercept and the process is unfeasible. In homogeneous batch distillation, the constraints of the material balance line does not hold. Considering a regular batch column, the column liquid profile (including the still composition and the distillate composition) can be represented by a residue curve under limiting conditions of high reflux and number of trays. Therefore, the process is feasible if, at any time, the still composition and the distillate composition are in the same batch distillation region.

In heterogeneous batch distillation, all reflux policies described above can be used and a feasible column profile is described by Eq. 4. Figure 4 shows the performance of a heterogeneous batch distillation process for the ternary mixture propyl formate−water−formic acid. This example illustrates how the still path can be steered thanks to the reflux policy so as to obtain pure formic acid at the end in the still. Case 1 with the sole reflux of the entrainer-rich phase is first considered. Subclasses 1.1, 1.2, and 1.3 are studied and the steering of the still path is presented, as well as the liquid column profile and the condensed vapor composition behavior. Simulation results obtained with Prosimbatch (Prosim, 1993) are presented considering 50 trays and all assumptions described above. Figure 4 displays the trajectory of the still composition along with examples of the still ($x_{s0},\ldots,x_{s3}$), condensed vapor ($y_{2,0},\ldots,y_{2,3}$), and second tray liquid ($x_{2,0},\ldots,x_{2,3}$) compositions during each step. Subscript number i,j indicates the tray and step numbers respectively. The main operational parameters are given in Table 1.

The heteroazeotrope is the only unstable node of the system. Hence, at total reflux a liquid column profile can always be achieved between any initial still composition and the hetroazeotropic point. As we have highlighted before, the liquid profile is strongly influenced by the vapor line. In this case, it drags the total reflux liquid profile into several batch distillation regions. For subcase 1.1, the entrainer-rich phase flow depends on the splitting ratio ω of the condensed vapor. When distillate removal begins, the still composition equals $x_{s,0}$, the entrainer-rich phase x_R is refluxed at the column top, and the liquid profile deviates abruptly from the one established at total reflux. As x_R is located in another batch distillation region than $x_{s,0}$, the liquid column profile crosses the batch distillation boundary and so does the still path during step 1 to continue its trajectory in a different batch distillation region until it reaches the formic acid vertex. Boundary crossing is a key property of heterogeneous batch distillation that produces more flexibility compared to homogeneous batch distillation in addition to more design alternatives and a far greater number of feasible ternary diagrams (Rodriguez-Donis et al., 2000b,c). Those authors have also shown that the use of a heterogeneous entrainer can reduce the number of batch distillation tasks. Finally, the entrainer-

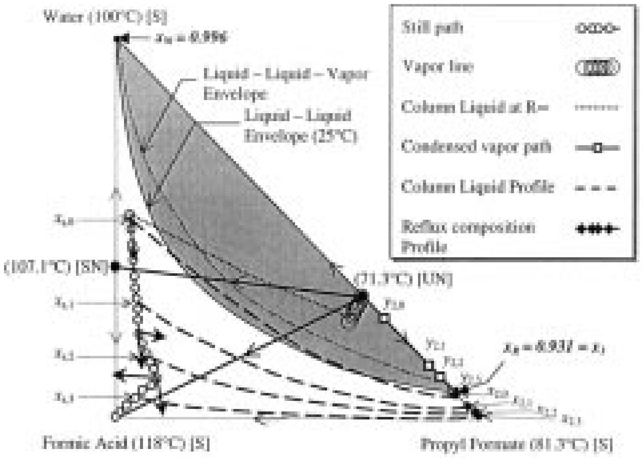

Figure 4. Simulation for heterogeneous batch distillation of water−formic acid using propyl formate and considering reflux of entrainer-rich phase.

Table 1. Reflux Policies for Separation by Heterogeneous Batch Distillation of a Water–Formic Acid Mixture Using Propyl Formate as Entrainer

Parameters		Reflux							
		Entrainer-Rich Phase Only				Both Phases			
No. of trays		50							
Initial charge (g)		500							
Initial composition		0.070/0.525/0.405							
Operating Pres. (atm)		1							
Efficiency of trays		1							
Boiler heat duty (W)		205							
Decanter vol. (mL)		50							
Step	$x_{s,\text{ at step end}}$	Subcase	ω	θ	φ	Subcase	ω	θ	φ
1	$x_{\text{propyl formate}} = 0.067$ $x_{\text{water}} = 0.210$	1.1	0.792 to 0.924	1.0	—	2.1	0.7237	1.0	0.4 to 0.8
2	$x_{\text{propyl formate}} = 0.114$ $x_{\text{water}} = 0.106$	1.3	0.924 to 0.958	1.01 to 1.036	—	2.3	0.7237	1.022	0.85
3	$x_{\text{propyl formate}} = 0.001$ $x_{\text{water}} = 0.004$	1.2	0.967 to 0.997	0.952 to 0.998	—	2.2	0.7237	0.967 to 0.998	0.926 to 0.998

rich phase left in the decanter can be recycled to the next batch process.

In Figure 4, during the first operational step, all the entrainer-rich phase that is contained in the overhead vapor is refluxed (subcase 1.1 with constant volume of the decanter entrainer-rich phase). Starting at $x_{s,0}$, the still composition follows a rectilinear line away from the composition of the weak-entrainer phase x_W and ends at $x_{s,\text{ at step end}}$ reported in Table 1. Later, the entrainer-rich phase reflux is increased (subcase 1.3), lowering the volume of the decanter entrainer-rich phase. The still trajectory lies into the vector cone delimited by vectors $(x_s - x_W)$ and $(x_R - x_s)$. During this second operational step, the entrainer concentration increases in the still to 11.4% in propyl formate (Table 1). Obviously, the entrainer-rich phase reflux must be decreased below the amount that is contained in the overhead vapor (subcase 1.2) so as to obtain pure formic acid in the still at the end of the process. The θ values for steps two and three are displayed in Table 1. As seen in Figure 4, the liquid column profile is mainly located in the homogeneous region once distillate removal starts. In particular, the liquid composition which leaves the second tray ($x_{2,0}$ to $x_{2,3}$) always lies in the homogeneous region and its corresponding equilibrium vapor $y_{2,0}$ to $y_{2,3}$ is not at the heteroazeotropic point, but somewhere in the 25°C liquid-liquid heterogeneous region so that a liquid-liquid phase split takes place in the decanter. Similarly to a continuous heterogeneous distillation process, the column can be operated as a homogeneous one while the process keeps its flexibility because the advantage of the partial liquid-liquid miscibility can still be used. In conclusion, a heterogeneous batch distillation process will be always feasible when the vapor composition that leaves the top of the column is inside the *demixion* region at the decanter temperature.

While the operation proceeds, the condensed vapor path moves toward the entrainer-rich phase composition (x_R) and a noticeable increase of the splitting ratio ω occurs as is shown in Table 1. Therefore, in the first step the entrainer-rich reflux flow must be increased to keep invariable its level in the decanter ($\theta = 1$). In the following steps, a high value of θ must be defined to guaranty a phase splitting of the overhead vapor in the decanter. Consequently, the distillate flow diminishes due to the high splitting ratio ω and the operation time is inevitably increased to reach the required purity in the still at the end of the process.

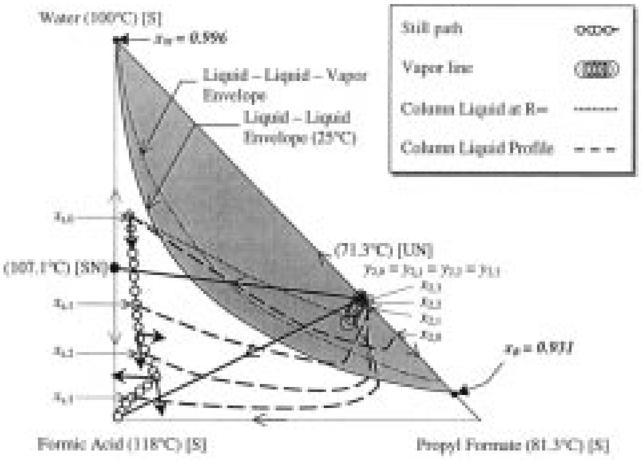

Figure 5. Simulation for heterogeneous batch distillation of water–formic acid using propyl formate and considering reflux of a combination of both decanted phases.

In order to keep a low splitting ratio ω, we consider a reflux policy involving the reflux of both phases. Identical initial and operating conditions are retained and the simulation results are displayed in Figure 5, considering the reflux policy corresponding to subcases 2.1, 2.2, 2.3. Each operational step finishes when the still reaches the same water composition than in the previous steps displayed in Figure 4 and reported in the $x_{s,\text{ at step end}}$ row of Table 1. As it happens, the propyl format composition at the end of each step is also similar in both cases. As seen in Table 1, the θ values for subcases 1.n and 2.n are comparable. Proportion of both refluxed phase (φ and θ) have to be increased in time to get a heterogeneous liquid stream leaving the first tray during the whole process. In this way, the heteroazeotropic mixture can boil overhead and the split ratio ω is then kept constant to its value at the heteroazeotropic composition. In general the ω

value can be kept constant if a liquid-liquid split takes place in the top tray of the column and its corresponding equilibrium vapor is located on the vapor line.

When both decanted phases are recycled, the overall composition of the liquid reflux is placed between the heteroazeotrope point and the entrainer-rich phase composition x_R that is in another batch distillation where the initial still composition is located. As a consequence, similar to the previous reflux policy, when distillation begins, the liquid column profile crosses the batch distillation boundary and the still path is able to visit several batch regions during its trajectory.

Overall, although they enable to reach a pure component vertex in the still at the end, both the entrainer-rich phase only and the combination of decanter phases reflux strategies have a negative effect on the productivity of the process due to the fact that the distillate flow diminishes in time. In the case of the entrainer-rich phase only reflux, this is due to the splitting ratio increase in time. In the case of a combination of both decanter phases reflux, this is due to a portion of the distillate (entrainer-weak phase) that is recycled to the column top. Hence, the operation time necessary to achieve the separation is consequently increased, affecting the cost of the process. In example displayed in Figure 4 and 5, the operation time with a combined reflux policy is higher than with the reflux of the entrainer-rich phase only. However, the reflux of both phases is likely easier to operate and control because the splitting ratio ω is constant and the drying of a decanted phase is unlikely to occur. Besides, we have found that when a combination of both phases is refluxed, less trays are needed to reach the heteroazeotropic composition. An optimal reflux policy can be found applying any optimization method and the best option will depend on the specific ternary system.

Improved Heterogeneous Batch Distillation Process

The use of a heterogeneous entrainer for the separation of an azeotropic mixture by batch distillation was first presented by Düssel and Stichlmair (1995) for the rectification of the pyridine-water mixture using toluene as an intermediate entrainer. Toluene forms a binary homoazeotrope with pyridine and binary heteroazeotrope with water. Three basic distillation regions are defined by two unstable curved separatrices sketched on Figure 6. For a rectifier configuration, the distillation region limited by the pyridine vertex is divided in two batch regions by a batch distillation boundary between this fixed point and the heterogeneous azeotrope, giving rise to four batch distillation regions. In this case, the initial ternary mixture (F_1) is obtained by adding toluene to the original binary mixture water-pyridine (F) so as to lie on the batch distillation boundary active for a rectifier operation. Assuming that homogeneous batch distillation synthesis methods under limiting conditions of high reflux and a large number of trays is valid, the authors determine the still path and the product sequence. A single batch rectifier is then required for the separation of both original components. The still path (α) shown in Figure 6 follows the batch distillation boundary toward the pyridine vertex whereas the heterogeneous binary azeotropic point (unstable node) is obtained as a product overhead. It behaves as in the homogeneous case where the still paths move linearly away from the distillation composition. The separation of water and toluene is near complete in the decanter thanks to the liquid-liquid phase split. At the end of the batch distillation, pyridine pure remains into the still.

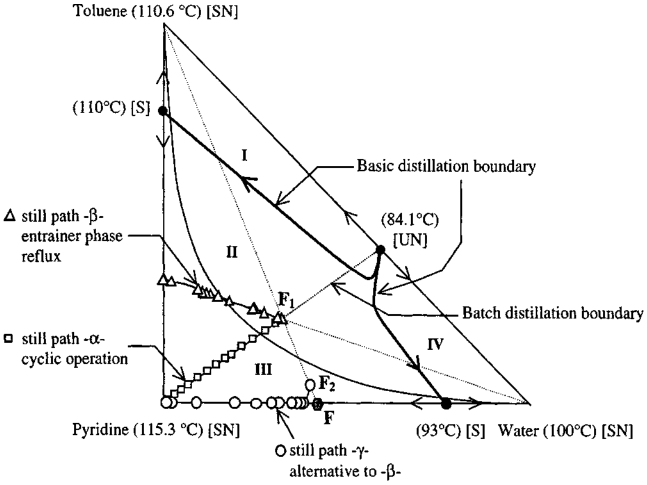

Figure 6. Separation of water–pyridine by heterogeneous batch distillation with toluene.

We have found that the rectilinear still path suggested by Düssel and Stichlmair does not correspond to the operation with a finite reflux of a regular heterogeneous column, as described in Figure 1. It rather matches the still path in a heterogeneous column that would be obtained for a cyclic operation (Sorensen, 1999) or the still path of a high finite reflux column which reflux is exactly the hetroazeotropic composition. If we consider a reflux of the entrainer phase only, the correct still path from feed F_1, noted as β on Figure 1, arrives at the pyridine-toluene side and a second batch rectifier task is compulsory to obtain pure pyridine. Path-β-includes the initial feed composition F_1 used by Düssel and Stichmair and is obtained by simulation of the process using ProSimBATCH, a commercial batch process simulator solving an equilibrium based model with heat effects included (Prosim, 1993). A column with 50 ideal trays is considered and the entrainer-rich phase reflux flow rate is calculated to keep a constant interface level and total level into the decanter. Estimations of liquid-vapor equilibrium, liquid-liquid-vapor equilibrium and liquid-liquid equilibrium are carried out using the thermodynamic model NRTL with binary parameters taken from the DECHEMA database (Gmehling and Onken, 1977).

A valuable result derived from this example is that the method for the synthesis of homogeneous batch distillation cannot be extended to heterogeneous systems without care. Indeed, there is a relationship between the initial amount of entrainer added to the original binary mixture F, the immiscibility region at the defined decanter temperature, the reflux policy used at the top of the column, and the number of batch tasks needed to obtain the two original components with a high purity. In fact, the initial amount of entrainer depends on the liquid holdup inside the column and the decanter and should be set such that the still contains none at the end of the process. Consequently, the reflux policy will be defined according to the entrainer composition in the still after the total reflux operation, as we have shown above. The simplest sequence of the process will be obtained when a relationship is established between the initial entrainer composition and the reflux policy used in the process as shown below.

Figure 1 shows the still path$-\gamma-$that illustrates a process for the separation of water-pyridine with toluene using the criteria anounced above. In this case, the addition of toluene to the original binary mixture (F) gives F_2 ternary mixture location in region III. The water-toluene heteroazeotrope is condensed at the column top and the water-rich phase in the decanter is withdrawn as distillate. Only the toluene-rich phase in the decanter is refluxed, with a flow rate imposed by the split ratio in the condensed vapor. In this example, the entrainer-weak phase x_R is almost pure toluene; hence, the still composition after the total reflux operation must be located on the binary side water-pyridine to assure that the still path reaches the pyridine vertex at the end of the process. The initial quantity of toluene and the imposed reflux policy permit that the toluene concentration in the still is almost negligible, while water is drawn as distillate during all operation. Using the same simulated column than before, the still path$-\gamma-$reaches the pure pyridine vertex and a single batch rectifier task is needed to perform the separation of both original components. Compared to the cyclic process discussed by Düssel and Stichlmair (1995), less entrainer is needed and there is no need to set the feed composition exactly on the batch distillation boundary.

Experiment and Simulation of Heterogeneous Batch Distillation Process

The feasibility analysis has been applied to another example and confirmed by simulation and experiments. This example is displayed in Figure 7 which shows the separation of acetonitrile-water using acrylonitrile as a light entrainer. The ternary system has two basic distillation regions divided by an unstable separatrix, which links the unstable heteroazeotrope with the saddle homoazeotrope acetonitrile-water. Besides, one of the basic regions can be divided by a batch distillation boundary in two batch distillation regions leading to a total of three batch distillation regions (I, II, III). The initial mixture F is situated in batch region III whose stable node is the water vertex. Feasibility analysis states that the heteroazeotropic composition should boil overhead and be split into the decanter in two phases, a water-rich phase and an acrylonitrile-rich phase. According to Eq. 4 and as illustrated in Figure 2b, if reflux policy 1.2 is used, the still path will be able to cross the distillation boundary and reach at the end of the process the stable node of region II, acetonitrile. If reflux policy 1.1 or 3.3 was used instead, the still path would arrive to the binary side acrylonitrile-acetonitrile instead of reaching the acetonitrile vertex according to the still trajectories established in Figure 2.

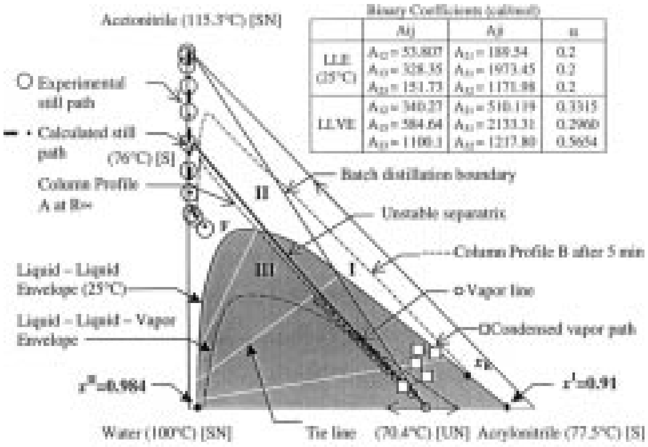

Figure 7. Separation of acetonitrile–water by heterogeneous batch distillation with acrylonitrile.

Case where the still path crosses the distillation boundary.

The column technical features and operating conditions are identical for the experiments and the simulations. The glass distillation column has a total height of 2.22 m and an internal diameter of 0.026 m. 77.4% of the total height is packed with stainless steel wire mesh rings and the remaining portion with glass Raschig rings 3×3 mm. The total packed height is considered to be equivalent to 50 theoretical plates

Table 2. Experimental and Simulated Results for Separation of Acetonitrile–Water Mixture Using Heterogeneous Batch Distillation

	Simulation Results			Experimental Results		
	Quantity (g)	Molar	Fraction	Quantity (g)	Molar	Fraction
	832.8	H_2O C_2H_3N C_3H_3N	0.434 0.510 0.055	832.8	H_2O C_2H_3N C_3H_3N	0.434 0.510 0.055
Heavy aqueous phase (P_1) (distillate + decanter)	230.1	H_2O C_2H_3N C_3H_3N	0.947 0.034 0.019	218.8	H_2O C_2H_3N C_3H_3N	0.9463 0.0349 0.0188
Light phase (decanter + pipes during experiments)	66.7	H_2O C_2H_3N C_3H_3N	0.122 0.166 0.715	60.15	H_2O C_2H_3N C_3H_3N	0.1796 0.1288 0.6916
Final still content (product P_2)	514.3	H_2O C_2H_3N C_3H_3N	0.002 0.992 0.006	496.2	H_2O C_2H_3N C_3H_3N	0.0041 0.9954 0.0005
C_2H_3N Mass recovery yield		95.6%			91.8%	

and a total liquid holdup of 52.5 mL. The initial charge and its composition are displayed in Table 2. Simulated boiler heat duty changes vs. time from 150 W until 135 W so as to match the experimental overhead vapor flow rate (12.0−12.5 mL/min). The condenser is subcooled to 25°C and the decanter capacity equals 70 mL. Pressure equals 1 atm and a 0.05 atm pressure drop is estimated.

Simulation of heterogeneous batch distillation is carried out with ProPhyPlus (properties server) and ProSimBatch (batch process simulator) (PROSIM, 1993). The NRTL thermodynamic model is used to represent phase equilibrium with binary parameters taken from the DECHEMA tables (Gmehling and Onken, 1977) and they are reported in Figure 7. Calculated equilibrium consistency is checked with ProPhyPlus against experimental data available in the literature (Gmehling and Onken, 1977). The liquid-liquid envelope at 25°C applies for the subcooled condenser and for the decanter. The column model consists of usual plate by plate MESH (Material balance, Equilibrium, Summation of factors and Heat balance) equations which are solved for the whole column, decanter included and taking into account the liquid-liquid demixion (Gmehling and Onken, 1997). Numerical treatment of the differential algebraic equation (DAE) system and discrete events handling is performed with DISCo, a numerical package for hybrid systems with a DAE solver based on Gear's method (Sargousse et al., 1999).

Simulations results are displayed in Figure 7 and Table 2. After the column is operated a few minutes under flooding conditions, total reflux operation is maintained during 1.5 h. The column liquid profile (A) at total reflux is close to the unstable separatrix, but 50 trays of the column are not enough to obtain the heteroazeotropic composition overhead. Later, the decanter is completely filled with condensed overhead vapor. The aqueous phase is removed, while the organic phase is refluxed into the column. Reflux policy 1.2 is used ($\theta = 0.935$) during the first 3.4 h in order for the still composition to end at the acrylonitrile vertex. 5 min after the distillation begins, the liquid profile B changes suddenly and crosses the unstable separatrix due to the recycle of the acrylonitrile-rich phase (Figure 7). With the additional drawing of the water-rich phase as distillate, the still path can transverse the unstable separatrix. After 6.4 h of such operation, high purity acetonitrile is left in the still. Besides, thanks to the reflux of an acrylonitrile-rich light phase, this compound is kept in the column and the overhead vapor remains heterogeneous during the whole process even though the liquid profile is mostly homogeneous. While the distillation proceeds, the number of trays in the column is not large enough to keep the condensed overhead vapor composition constant. However, the process is always feasible because a liquid-liquid split occurs in the decanter with the splitting ratio value ω growing from 0.853 to 0.99 at the end of the batch distillation. Accordingly, the distillate water content on the tie line corresponding to the overhead vapor is progressively reduced. Although its time averaged value is acceptable ($x = 0.947$), it may require further purification.

Experiments taking into account these operational conditions are carried out in the laboratory column and the results are presented in Figure 7 and Table 2. Analysis of the still composition is performed every hour. Analysis of the decanter content (organic and aqueous phase) and the distillate product are made at the end of the operation (6.4 h). The water, acetonitrile, and acrylonitrile compositions were determined using a SHIMADZU gas chromatography configured with TC detector and two columns packed with Cromasorb 101 (2.1 m × 2.6 mm). The injector and detector temperature were held at 170°C, while the column temperature was assigned to be constant 120°C. The carrier gas (helium, grade 5.6) flow rate is maintained at 36 cm^3/min. Prior calibration was done using internal standards in samples prepared by mass on a SARTORIUS BP 211D balance with a precision of 10 μg. The standard accuracy and reproducibility in the composition for all components are found to be $\pm 0.1\%$ and 0.3%, respectively. The water composition was also corroborated by the Karl Fisher technique.

As can be seen in Figure 7, the still path obtained by experimentation agrees very well with the trajectory calculated by simulation. Table 2 displays the quantity and composition of the main streams of the process. Water is drawn off as a distillate product with a molar composition of .946%. 99.6% acetonitrile is recovered in the still at the end of the process. The amount of acrylonitrile needed for this operation is low and the makeup of the fresh solvent for a next cycle of water-acetonitrile separation is approximately 30%.

Conclusion

A feasibility analysis is conducted in this article for the separation of azeotropic mixtures by heterogeneous batch distillation in a batch rectifier. A mathematical model based on the simplifying assumptions of constant molar overflow and quasi steady state on the trays of the column is developed. This model is then used for the calculation of the still path and the rectifying column profile considering six different reflux policies covering all combination of both decanted phase flow rates. Depending on the reflux policy, the still trajectory follows a straight line or its motion is bounded by a vector cone until it reaches either a vertex or the edge on the triangle. The combination of several reflux policies allows steering the still pot composition by varying the relative weight of both vectors that restrict the still path.

In heterogeneous batch distillation, feasibility means that there is at least one liquid profile connecting each punctual composition on the still x_S path with the liquid composition leaving the first tray x_1 whose equilibrium vapor lies in the immiscibility gap at the decanter temperature. This necessary and sufficient condition must hold during both total reflux and distillation steps of the batch rectifier. During total reflux operation, a column liquid profile will connect the initial still composition to the heteroazeotrope boiling overhead if the initial composition is located in the same basic distillation region as the unstable binary heteroazeotrope. In this case, the column profile deviates from the simple distillation residue curve in the homogeneous region, as it hits the heteroazeotrope through the vapor line. When the distillate removal step begins, the feasibility condition is achieved using any of the reflux policies. For all of them, the liquid reflux composition is located in a different distillation region than the still composition. Therefore, the still path is able to cross the distillation boundary because of two factors: removal of the entrainer-weak phase as a distillate product and the reflux of the decanted phases at the top of the column. A suitable reflux policy can be found applying any optimization method and the best option will depend on the specific ternary system.

Simulation results confirm that the feasibility method employed in homogeneous batch distillation, considering total reflux and a high number of trays to determine the still path and distillate cut sequences, cannot be straightforward when extended to a heterogeneous batch distillation process. Indeed, it acts like a self-sustained continuous feeding batch distillation due to the differences in compositions of the liquid reflux and of the condensed vapor leaving from the column which are alike.

Application of the feasibility analysis to the separation of acetonitrile-water with acrylonitrile by heterogeneous batch distillation show that its conclusions are corroborated by rigorous simulations and experiments. A little amount of entrainer can be added and an appropriate reflux ratio policy allows the still path to cross batch distillation boundaries. The separation of both original components can be performed using a single batch rectifier where the component miscible with the entrainer is recovered in the distillate, while the other original component is obtained in the still at the end of the process.

Acknowledgment

This work was financially supported by the ALFA-Programme of the European Community. Its contribution was indeed highly appreciated.

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Manuscript received July 24, 2001.